Metrohm
Ion analysis

Trace-Level Determination of Bromate in Water by Ion Chromatography with Optimized Post-Column Derivatization and UV/vis Detection as Triiodide

Achim Rumi,[1] Rob Proost[2] and Alfred Steinbach[1]
[1]Metrohm AG, [2]Applikon BV

During recent years, the necessity to determine bromate in drinking and mineral waters has increased significantly because bromate is a potential carcinogen. Bromate is generated by the oxidation of bromide traces during water disinfection, for example by ozonization. The US Environmental Protection Agency (US EPA) and the European Union (EU) currently prescribe a maximum bromate concentration of 10 parts per billion (ppb) in drinking water. For mineral waters the pertinent regulations stipulate a limit of 3 ppb.

To satisfy the regulatory requirements, the determination of bromate needs very sensitive analytical methods. The most widely used methods for the quantification of bromate are based on anion-exchange chromatography (AEC). While conductivity detection suffers from relatively high detection limits (0.1–20 ppb), the coupling of ion chromatography (IC) with mass spectrometry (MS) achieves an outstanding 6 parts per trillion (ppt) detection limit (1). However, MS detection is a rather demanding and costly technique. For this reason several sensitive post-column reactions (PCRs) followed by spectrophotometric detection have been investigated. The post-column derivatization of bromate with o-dianisidine (ODA) according to EPA method 317 achieves a detection limit of approximately 0.2 ppb (1), but the use of potentially carcinogenic ODA is a major drawback. The alternative EPA method 326 stipulates post-column reaction of bromate with the less harmful iodide under acidic conditions. Bromate oxidizes the iodide to the triiodide ion. The latter is detected at 352 nm. The aqueous sample can be directly injected without any sample preparation other than filtration.

This paper presents the results of the optimization of the PCR with respect to temperature, eluent composition and iodide concentration.

The Triiodide Method

As already mentioned, the analysis is based on the EPA method 326. In this post-column derivatization method, bromate — aided by the catalytic effect of ammonium molybdate — oxidizes iodide to triiodide in an acidic medium according to Equations 1–4. According to Equation 4 the bromate anion is “stoichiometrically amplified” by a factor of three.

$$\mathrm{BrO_3^- + 3I^- + 3H^+ \xrightarrow{[Mo(VI)]} 3HOI + Br^-} \qquad [1]$$

$$\mathrm{3HOI + 3I^- + 3H^+ \longrightarrow 3I_2 + 3H_2O} \qquad [2]$$

$$\mathrm{3I_2 + 3I^- \longrightarrow 3I_3^-} \qquad [3]$$

$$\mathrm{BrO_3^- + 9I^- + 6H^+ \xrightarrow{[Mo(VI)]} Br^- + 3I_3^- + 3H_2O} \qquad [4]$$

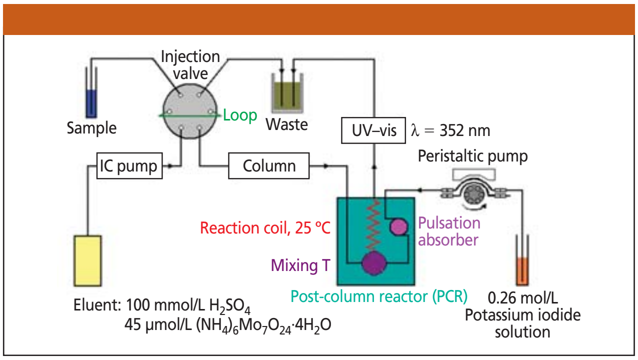

Figure 1: Schematic illustration of the IC system.

The reaction rate of Equation 1 is only high enough with molybdate(VI) catalysis and at high sulphuric acid concentrations. However, direct acidification of the KI solution enhances the oxidation of iodide by oxygen and results in the formation of interfering yellowish triiodide anions (2). While this problem is frequently solved by on-line acidification via a micromembrane suppressor, installed just before the mixing T and the reaction coil (3,4), we used a sulphuric acid eluent with catalytic amounts of ammonium molybdate (Figure 1). This means that only the potassium iodide solution has to be added as derivatization reagent. This method is ideally suited for the selective determination of bromate and it is not affected by other drinking water matrix anions.

Modifications of the presented set-up using a carbonate/hydrogen carbonate eluent and two different post-column reagents, as described by Bogenschütz et al. (5) and in Metrohm Application Note U-9 (6), allow the simultaneous spectrophotometric detection of iodate, chlorite, bromate and nitrite. These anions specifically oxidize iodide to the triiodide anion in acidic solution. In contrast, other strong oxidants such as chlorate and perchlorate do not react with iodide under the given conditions and are therefore best determined by suppressed conductivity and/or MS detection. If a conductivity detector is combined with post-column reaction and subsequent UV detection, water matrix anions (chloride, nitrate, sulphate, etc.), oxyhalides (BrO_3^-, IO_3^-, ClO_2^-) and nitrite can be detected in a single run.

Experimental

Post-column reaction: The post-column reaction was accomplished in the Metrohm IC Post-Column Reactor (Metrohm AG, Herisau, Switzerland). A peristaltic pump transfers the KI solution with a flow-rate of 0.25 mL/min to the reaction coil of the PCR (with a volume of 0.4 mL) where it is mixed with the column’s acid effluent stream. A built-in pulsation absorber ensures a stable reagent flow. As shown in Figure 1, the generated triiodide is subsequently conveyed to the ultraviolet/visible (UV/vis) detector where it is detected with a molar extinction coefficient of 26400 L/(mol·cm) at a wavelength of 352 nm.

Instrumentation: All experiments were performed on the 844 Compact UV/vis ion chromatograph (Metrohm AG) using the Star Ion A300 HC column (Phenomenex Inc., Torrance, California, USA). In all experiments the flow-rate of the mobile phase was 1 mL/min and the injection volume 1000 µL. Instrument control, data acquisition and processing were done by IC Net software (Metrohm AG).

Standard solutions, post-column reagents and eluents: All reagents used in this work were of the highest purity grade (puriss p.a.). Potassium iodide, the potassium bromate standard, the sulphuric acid and ammonium molybdate were all purchased from Fluka (Sigma-Aldrich, Buchs, Switzerland). All solutions were prepared with deionized water with a specific resistance higher than 18 MΩ·cm.

Results and Discussion

This article deals with the influence of temperature, molybdate and sulphuric acid concentration of the eluent as well as potassium iodide concentration on the performance of the triiodide method. While one of these parameters was varied, the detector response of a 1000 µL direct injection of a 10 ppb bromate standard was recorded. By applying the optimized conditions, a tap water sample from Herisau (Switzerland) was analysed for bromate.

Influence of temperature

For the adjusted potassium iodide flow-rate of 0.25 mL/min, the variation of the PCR's temperature only slightly affects the "bromate peak" (Figure 2). Thus the post-column derivatization, as reported by Salhi and von Gunten (3), can be performed at a reaction coil temperature of 25 °C. According to Wagner et al. (7) higher flow-rates require an increased post-column reactor volume and/or a higher reaction coil temperature.

Influence of eluent composition

a) Ammonium molybdate

No significant enhancement in sensitivity was observed for concentrations exceeding 45 µmol/L ammonium molybdate. Lower concentrations result in a loss of sensitivity. Accordingly, the remaining tests were performed with an ammonium molybdate concentration of 45 µmol/L.

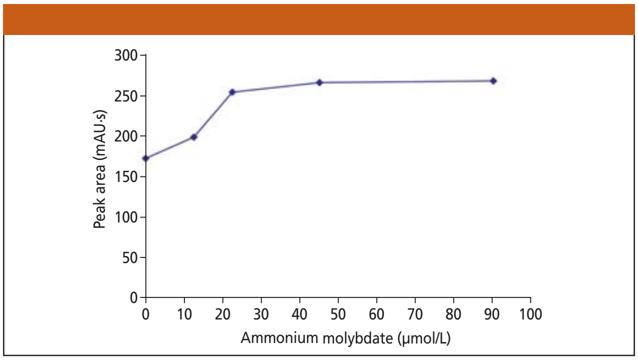

Figure 3: Detector response for 10 ppb bromate as a function of ammonium molybdate concentration (0, 12.5, 22.5, 45 and 90 µmol/L). Each measuring point corresponds to the mean value of five determinations.

b) Sulphuric acid

By varying the concentration of sulphuric acid in the eluent, the influence on the "bromate peak" can be evaluated (Figure 4).

No sensitivity improvement was obtained for sulphuric acid concentrations above 31 mmol/L. Below this threshold value the response of the "bromate peak" decreases rapidly. Additionally, increasing pH results in increased retention times, which means longer analysis times. The remaining tests were performed with a sulphuric acid concentration of 100 mmol/L.

Influence of iodide concentration

To examine the effect of the potassium iodide concentration on the formation of the triiodide ion, the potassium iodide concentration was varied between 0.26 and 0.75 mol/L.

In the range investigated, the variation of the iodide concentration has no significant effect on the sensitivity of the triiodide method (Figure 5).

Analysis of tap water

The optimized conditions summarized in Table I were applied to bromate determination in a tap water sample from Herisau

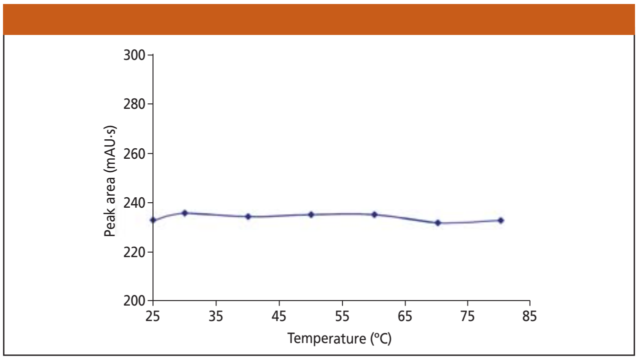

Figure 2: Detector response for 10 ppb bromate as a function of temperature (25, 30, 40, 50, 60, 70, and 80 °C) in the reaction coil of the PCR. Each measuring point corresponds to the mean value of four determinations.

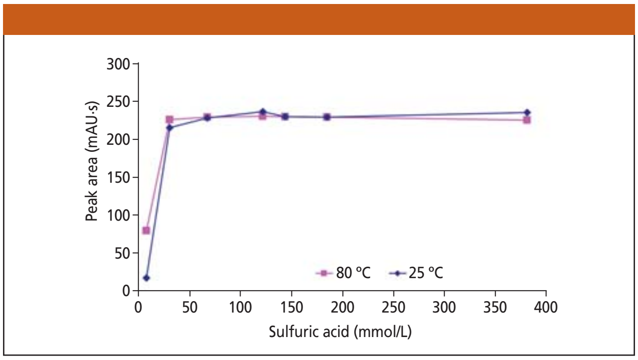

Figure 4: Detector response for 10 ppb bromate as a function of sulphuric acid concentration (8, 31, 68, 122, 144, 185 and 381 mmol/L). Each measuring point corresponds to the mean value of three determinations.

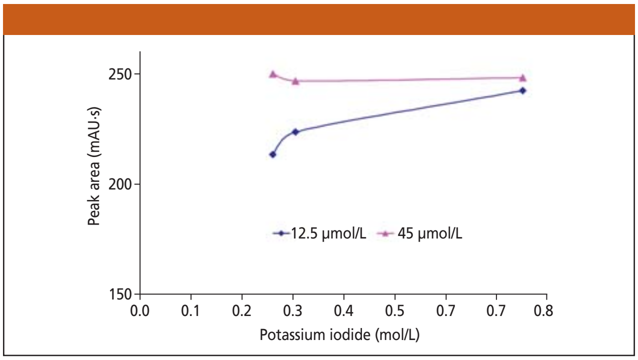

Figure 5: The detector response for 10 ppb bromate as a function of potassium iodide concentration (0.26, 0.305, and 0.75 mol/L). The ammonium molybdate (45 µmol/L) and sulphuric acid concentration (100 mmol/L) in the eluent were held constant. Each measuring point corresponds to the mean value of three determinations.

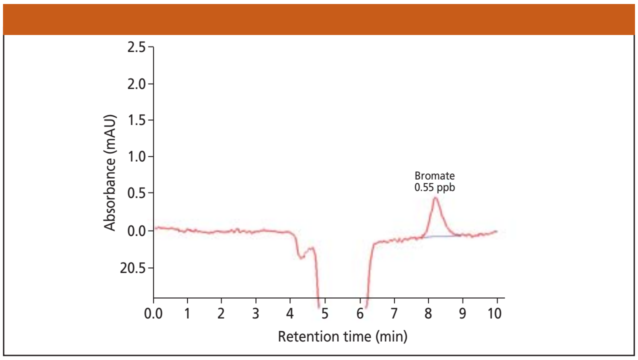

Figure 6: UV anion chromatogram of tap water from Herisau (Switzerland).

(Switzerland). The peak of the UV chromatogram in Figure 6 corresponds to a bromate concentration of 0.55 ppb.

Conclusions

Bromate can be determined at trace levels by anion-exchange chromatography followed by post-column derivatization with subsequent UV detection, according to US EPA Method 326. The straightforward set-up uses a sulphuric acid eluent with catalytic amounts of ammonium molybdate and requires neither suppression nor sample preparation steps. The bromate response was neither dependent on the investigated reaction temperatures (25…80 °C) nor on the examined iodide concentrations (0.26…0.75 mol/L KI). In contrast, the molybdate and sulphuric acid concentrations had a significant influence on method sensitivity. Increasing sulphuric acid concentrations (> 31 mmol/L) improved sensitivity and shifted the "bromate peak" to shorter retention times. Ammonium molybdate concentrations of 45…90 µmol/L in the eluent yielded the best results. Applying the optimum conditions for the triiodide method, a detection limit for bromate of less than 50 ng/L (= 50 ppt) is achieved.

References

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(5) G. Bogenschütz et al., Advanced detection techniques in ion chromatography, Metrohm Monograph, Herisau, Switzerland (2007) in press.
(6) Metrohm Application Note No. U-9, Iodate, chlorite, bromate and nitrite by suppressed ion chromatography applying post column reaction (PCR) and UV/vis detection.
(7) H.P. Wagner et al., *J. Chromatogr., A* **956,** 93–101 (2002).

Table I: Ion chromatographic and post-column reaction conditions for the determination of bromate.

Analytical column	Phenomenex Star Ion A300 HC
Eluent	100 mmol/L sulphuric acid 45 µmol/L ammonium molybdate
Flow-rate	1 mL/min
Sample loop volume	1000 µL
Post-column reagent	0.26 mol/L potassium iodide
Reaction coil volume	0.4 mL
Potassium iodide flow rate	0.25 mL/min
Post-column temperature	25 °C
UV detector cell wavelength	352 nm